

**OFFICE OF NAVAL RESEARCH**  
**FINAL REPORT**  
**PUBLICATIONS/PATENTS/**  
**PRESENTATIONS/**  
**HONORS/STUDENTS**

*for*

*GRANT NO: N00014-95-1-0717*

*PR Number: 96PR01783; 3134074*

**ATOMIC LAYER EPITAXY OF**  
**SUPERCONDUCTING**  
**OXIDES AND**  
**HETEROSTRUCTURES**

*R.P.H. Chang & Tobin J. Marks*

*Northwestern University*

*Department of Materials Science & Engineering*

*Department of Chemistry*

*2225 N. Campus Dr., 2145 Sheridan Rd*

*Evanston, IL 60208*

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**OFFICE OF NAVAL RESEARCH**

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**PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT****PR Number:** 96PR01783**Contract/Grant Number:** N00014-95-1-0717**Contract/Grant Title:** Atomic Layer Epitaxy of Superconducting Oxides & Heterostructures**Principal Investigators:** R.P.H. Chang & Tobin J. Marks**Mailing Address:** 2225 N. Campus Dr., Evanston, IL 60208-3108**Phone Number:** (847)491-3598; (847)491-5658**Fax Number:** (847)491-4181**E-mail Addresses:****http address:****PART I****A.** Number of papers submitted to refereed journals, but not published: 7**B.** + Number of papers published in refereed journals: 14**C.** + Number of books or chapters submitted, but not yet published: 0**D.** + Number of books or chapters published (for each, provide a complete citation): 1**E.** + Number of printed technical reports/non-refereed papers (for each, provide a complete citation):  
0**F.** Number of patents filed: 2**G.** + Number of patents granted (for each, provide a complete citation): 0**H.** + Number of invited presentations (for each, provide a complete citation): 14**I.** + Number of submitted presentations (for each, provide a complete citation): 8**J.** + Honors/Awards/Prizes for contract/grant employees (list attached):

(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)

**K.** Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: 3.5

Graduate Students: 1

Post-Doctoral Associates: 2.5

including the number of,

Female Graduate Students: 0

Female Post-Doctoral Associates: 0

Minority\* Graduate Students: 0

Minority\* Post-Doctoral Associates: 0

Asian Graduate Students: 1

Asian Post-Doctoral Associates: 1

#### **A. Papers Submitted to Refereed Journals and not yet published**

1. Buchholz, D.B.; Marksworth, P.R.; Belot, J.A.; Marks, T.J.; Chang, R.P.H., The Effect of Growth Conditions on the Composition of YBCO Thin Films Grown by Pulsed Organo-Metallic Beam Epitaxy, submitted to *Appl. Phys. Lett.*
2. Buchholz, D.B.; Marksworth, P.R.; Belot, J.A.; Marks, T.J.; Chang, R.P.H. The Effect of the Film-Substrate Interface Layer on the Properties of YBCO grown on LaAlO<sub>3</sub>, MgO, and YSZ by Pulsed Organo-Metallic Beam Epitaxy, submitted to *Phys. Rev Lett. B*.
3. Belot, J.A.; Wang, A.; McNeely, R.J.; Liable-Sands, L.; Rheingold, A.L.; Marks, T.J. Liquid Lanthanides. Volatile, Low Melting, Fluorine-Free Precursors for Metal-Organic Chemical Vapor Deposition of Thin Metal Oxide Films, submitted for publication.
4. Wang, A.; Dai, J.; Cheng, J.; Chudzik, M.P.; Marks, T.J.; Chang, R.P.H.; Kannewurf, C.R. Charge Transport, Optical Transparency, Microstructure, and Processing Relationships in Transparent Conductive Indium-Zinc Oxide Films Grown By Low Pressure Metal-Organic Chemical Vapor Deposition, *Appl. Phys. Lett.*, in press.
5. Wang, A.; Belot, J.A.; Marks, T.J. Film Microstructure - Deposition Condition Relationships in the Growth of Epitaxial NiO Films by MOCVD on Oxide and Metal Substrates, *J. Mater. Res.*, in press.
6. Neumayer, D.A.; Belot, J.A.; Feezel, R.L.; Reedy, C.; Stern, C.L.; Marks, T.J.; Liable-Sands, L.M.; Rheingold, A.L. Approaches to Alkaline Earth Metal-Organic Chemical Vapor Deposition Precursors. Synthesis and Characterization of Barium Fluoro--Ketoiminate Complexes Having Appended Polyether "Lariats", *Inorg. Chem.*, in press.
7. Belot, J.A.; McNeely, R.J.; Wang, A.; Reedy, C.J.; Marks, T.J.; Yap, G.; Rheingold, A.L. Expedient Route to Volatile Zirconium Metal-Organic Chemical Vapor Deposition Precursors Using Amide Synthons and Implementation in Yttria-Stabilized Zirconia Film Growth, *J. Mater. Res.*, in press.

#### **B. Papers Published in Refereed Journals**

1. "Stability of Bilayer Films of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and Y-ZrO<sub>2</sub> Grown on LaAlO<sub>3</sub> by Pulsed

Organometallic Beam Epitaxy," Forrest H. Kaatz, Paul R. Markworth, Ji-Yan Dai, D. Bruce Buchholz, Xiang Liu, Michael P. Chudzik, John A. Belot, Carl R. Kannewurf, Tobin J. Marks, and Robert P.H. Chang, *Chem. Vap. Deposition* , **4**, 99 (1998).

2."Electron Microscopy Study of Interfacial Structure and Reaction of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>/Y-ZrO<sub>2</sub> films on LaAlO<sub>3</sub> Substrates," J.Y. Dai, F.H. Kaatz, P.R. Markworth, D.B. Buchholz, X. Liu, W.A. Chiou, and R.P.H. Chang, *J. Mater. Res.* , **13**, 1485 (1998).

3."The Effect of Reactant Gas on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> Film Formation," D.B. Buchholz, P.R. Markworth, J.A. Belot, T.J. Marks, and R.P.H. Chang, *Matls. Chem. & Phys.* , **50**, 166 (1997).

4."The Growth of (001) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> Thin Films on (001) MgO by Pulsed Organo-Metallic Beam Epitaxy with Controlled In-Plane Orientation," D.B. Buchholz, J.S. Lei, S. Mahajan, R.P.H. Chang, B. Hinds, T.J. Marks, Y. Huang, and K.L. Merkle, *J. of Alloys & Compounds* , **251**, 278 (1997).

5."Efficient Route to TlBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>9+3</sub> Thin Films by Metal-Organic Chemical Vapor Deposition Using TlF as a Thallination Source, R.J. McNeely, J.A. Belot, B.J. Hinds, T.J. Marks, J.L. Schindler, M.P. Chudzik, C.R. Kannewurf, X.F. Zhang, and D.J. Miller, *Appl. Phys. Lett.* , **71**, 1243 (1997).

6."Liquid Source Metal-Organic Chemical Vapor Deposition of High-Quality YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Films on Polycrystalline Silver Substrates," D.B. Studebaker, J. Zhang, T.J. Marks, Y.Y. Wang, V.P. Dravid, J.L. Schindler, and C.R. Kannewurf, *Appl. Phys. Letts.* , **72**, 1253 (1998).

7."Volatility by Design. Synthesis and Characterization of Polyether Adducts of Bis(1,1,1,5,5,5-Hexafluoro-2,4-Pentadionato) Barium and Their Implementation as Metal-Organic Chemical Vapor Deposition Precursors," John A. Belot, Deborah A. Neumayer, Charles J. Reedy, Daniel B. Studebaker, Bruce J. Hinds, Charlotte L. Stern, and Tobin J. Marks, *Chemistry of Materials* , **9**, 1638 (1997).

8."The Growth of a-axis Normal YBCO Thin Films by Pulsed Organo-Metallic Beam Epitaxy," D.B. Buchholz, P.R. Markworth, J.A. Belot, T.J. Marks, and R.P.H. Chang, *J. of Mater. Res.*, **68**, 3037 (1996).

9."Fabrication and Characteristics of Weak Links Between and a -axis Normal Grains, S. Mahajan, D.B. Buchholz, J. Lei, T. Hogan, S.N. Song, B. Hinds, C.R. Kannewurf, T.J. Marks, J.B. Ketterson, J. Eckstein, and R.P.H. Chang, *J. Mater. Res.* , **11** (1996) 1086

10."Thin Films for Superconducting Electronics. Precursor Performance Issues, Deposition Mechanisms, and Superconducting Phase Formation-Processing Strategies in the Growth of Tl<sub>2</sub>Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> Films by Metal-Organic Chemical Vapor Deposition, B.J. Hinds, R.J. McNeely, D.L. Studebaker, T.J. Marks, T.P. Hogan, J.L. Schindler, C.R. Kannewurf, X. Zhang, and D.J. Miller, *J. Mater. Res.* , **12**, 1214 (1997).

11."MOCVD Precursor Design Issues. Recent Advances in the Chemistry and Vapor Pressure Characteristics of Ba(hexafluoroacetylacetonate)<sub>2</sub>polyether Complexes," T.J. Marks, J.A. Belot, C.J. Reedy, R.J. McNeely, D.B. Studebaker, D.A. Neumayer, and C.L. Stern, *J. Alloys. Cmpds* , **251**, 243 (1997).

12."MOCVD Routes to Tl-2212/MgO/Tl-2212 Trilayers. Preliminary Observations On Growth and Microstructural/Electrical Properties, B.J. Hinds, R.J. McNeely, J. Chen, C. Dias, D.B. Studebaker, T.J. Marks, T.P. Hogan, J.L. Schindler, and C.R. Kannewurf, *J. Alloys. Cmpds* , **251**, 328 (1997).

13."New Materials for Superconducting Electronics. Epitaxial Growth of LaSrGaO<sub>4</sub> and PrSrGaO<sub>4</sub>

Dielectric Thin Films by Metal-Organic Chemical Vapor Deposition," J.A. Belot, B.J. Hinds, J. Chen, Y.-Y. Wang, V. Dravid, and T.J. Marks, *Chem. Vap. Deposition* **3**, 78 (1997).

14. "In-Plane Orientation Control of (001)YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Grown on (001)MgO By Pulsed Organometallic Beam Epitaxy", Buchholz, D.B.; Lei, J.S.; Mahajan, S.; Markworth, P.R.; Chang, R.P.H.; Hinds, B.; Marks, T.J.; Schindler, J.L.; Kannewurf, C.R.; Huang, Y.; Merkle, K.L. *Appl. Phys. Lett.* **1996**, *68*, 21.

### **C. Book chapters submitted, but not published:**

Marks, T.J.; Belot, J.A.; Hinds, B.J.; Chen, J.; Studebaker, D.; Lei, J.; Chang, R.P.H.; Schindler, J.L.; Kannewurf, C.R. MOCVD Routes to Thin Films for Superconducting Applications. Precursor Synthesis and Film Processing Issues, *Mats. Res. Soc. Sympos. Proc.* **1996**, *415*, 67.

### **D. Book chapters published**

Shulz, D.L.; Marks T.J. Superconducting Materials, in *CVD of Non-Metals*, W. Rees, ed., VCH Publishers, New York, **1996**, 39-150.

### **G. Licensing Agreements**

"Precursors for Ba MOCVD", Medichem Inc.

Confidentiality Agreements

With all members of the ARPA HTMA

With Intermagnetics General Corp.

### **H. Invited Presentations**

#### **T.J. Marks**

1. "MOCVD Routes to Metal Oxide Films for Superconducting Applications and Other Applications"
2. 6/95 ISTE-MRS Superconducting Materials Workshop (Maui), "MOCVD Routes to Films for Superconducting Electronics."
3. 8/95 EURO-CVD (Venice), "MOCVD Routes to Films for Superconducting Electronics"
4. 10/95 Oak Ridge National Laboratory, "MOCVD Routes to Films for Superconducting Electronics"
5. 11/95 Materials Research Society Fall Meeting (Boston)
6. 6/96 "Metal-Organic Chemical Vapor Deposition Routes to Metal Oxide Films for Superconducting Electronics and Other Applications," European MRS Meeting (Strasbourg)
7. 8/96 "Metal-Organic Chemical Vapor Deposition Routes to Metal Oxide Films for Superconducting Electronics and Other Applications," MISCON Summer School on HTS Film Growth and Characterization (Notre Dame)
8. 1/97 "Metal-Organic Chemical Vapor Deposition Routes to Metal Oxide Films for Superconducting Electronics and Other Applications," Elf-Atochem Laboratories (King of Prussia)
9. 4/97 "Metal-Organic Chemical Vapor Deposition Routes to Metal Oxide Films for Superconducting Electronics and Other Applications," American Chemical National Meeting (San Francisco)
10. 11/97 Materials Research Society Fall Meeting (Boston)
11. 4/98 U. of California, Berkeley

**R.P.H. Chang**

1. 7/98 NSF-CNRS Workshop on High Temperature Superconductors (Caen)
2. 7/98 DOE Workshop on Coated Conductors (Dulles)
3. 1/97 "Advances in the Synthesis of Complex Oxide Films and Carbon Films", R.P.H. Chang, Academia Sinica, Taiwan
4. 5/97 "The Growth of YBCO Thin Films by Pulsed Beam Epitaxy," Department of Materials Science & Engrg., University of Michigan, Ann Arbor, MI.

**I. Submitted Presentations**

1. 11/95 Materials Research Society Fall Meeting (Boston, two symposia).
2. 4/96 "Properties of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Grain Boundary Junctions on LaAlO<sub>3</sub> (100) and MgO (100) Substrates," S. Mahajan, D.B. Buchholz, J. Lei, R.P.H. Chang, S.N. Song, J.B. Ketterson, B. Hinds, and T. Marks, April 1996, MRS Spring 1996 Meeting, San Francisco, CA.
3. 4/96 "Control of the In-Plane Orientation of (001) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Deposited on (001) Mg)," D.B. Buchholz, S. Mahajan, J.L. Schindler, C.R. Kannewurf, T.J. Marks, B. Hinds, and R.P.H. Chang, April 1996, MRS Spring 1996 Meeting, San Francisco, CA.
4. 4/96 "In-Situ Characterization of Composition and Oxygen Incorporation During Ion Beam Deposition of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>," A.R. Krauss, O. Auciello, J. Im, Y.Z. Hu, E.A. Irene, G.E. McGuire, V.S. Smentkowski, D.M. Gruen, and R.P.H. Chang, Symposium Q, Materials Challenges for Applications of High-Temperature Superconductors, April 1996, MRS Spring 1996 Meeting, San Francisco, CA.
5. 6/96 "Recent Results on Pulsed Organo Metallic Beam Epitaxy of YBCO," D.B. Buchholz, J. Lei, S. Mahajan, P. Markworth, R.P.H. Chang, S.N. Song, J.B. Ketterson, B. Hinds, and T.J. Marks, E-MRS Spring Meeting, Strasbourg FRANCE.
6. 5/97 International Workshop on Thallium Superconductors (Cambridge)
7. 6/97 ISTE-C-MRS Workshop on High Temperature Superconductors (Kona), Japan
8. 12/97 "The Effect of the Interfacial Seed Layer on the Crystal Quality of Oxide Thin Films Grown by Organo-Metallic Chemical Vapor Deposition," P.R. Markworth, X. Liu, D.B. Buchholz, R.P.H. Chang, J. Belot and T.J. Marks, MRS Fall Meeting, Nov. 30- Dec. 5, 1997, Boston, MA.

**J. Honors/ Awards/ News Articles****T.J. Marks**

1. 1996 Kilpatrick Lecturer, Illinois Institute of Technology
2. 1997 Royal Society of Chemistry Centenary Medallist and Lecture
3. 1997 Siedle Lecturer, Indiana U.
4. 1998 Francis Clifford Phillips Lecturer, U. of Pittsburgh
5. 1998 Seaborg Lecturer, U. of California, Berkeley
6. 1998 Closs Lecturer, U. of Chicago
7. Editorial Advisory Board, *Advanced Materials*, CVD
8. Editorial Advisory Board, *Journal of Molecular Catalysis*
9. 1999 Abbott Lecturer, U. of North Dakota
10. 1999 Marcus Lecturer, Washington U.
11. Chair, ACS Division of Inorganic Chemistry
12. Technical Advisory Board, Dow Corning Corp.
13. Technical Advisory Board, Dow Chemical Co.
14. DOE-BES Council on Chemical Sciences
15. Task Force, ACS Review of *Inorganic Chemistry*

**R.P.H. Chang**

Chairman of Advisory Committee to Materials Research Laboratory, ITRI, Hsinchu, Taiwan, 1997

Member at Large of the International Union of Pure and Applied Physics, 1997

Member of the Materials Education Council, 1996, 1997

## **K. Personnel**

**Research Associates:** Dr. Forrest Kaatz and Dr. John Belot, Dr. Anchuan Wang and **Graduate Students:** Xiang Lui, Eric Seelig, were supported during the year.

# **PART II**

**A. Principal Investigators:** R.P.H. Chang & Tobin J. Marks

**B. Current telephone number:** (847)491-3598; (847)491-5658

**C. Cognizant ONR Scientific Officer:** Dr. John C. Pazik

## **D. Brief Description of Project**

This project focuses on optimizing/understanding the growth and properties of YBCO, TBCCO, and lattice-matched dielectric films as well as YBCO superlattices by MOCVD and POMBE. Emphasis is on bulk film properties as well as film growth, interface evolution, and in situ studies of film growth processes.

### **Program Objective**

The objective of this program is to create via novel means and to understand the properties of interfacial growth regions between films of high-temperature superconducting (HTS) materials and insulating metal oxides. Improving the nature of such interfaces is a crucial barrier which must be surmounted before HTS materials can be successfully incorporated on a large scale into a myriad of advanced active and passive electronic device technologies. In addition, low melting-point advanced precursors are to be designed and synthesized for large scale HTS production. Studies of vapor transport properties and stabilities are carried out to assure that these precursors are of HTS manufacturing quality.

## **Accomplishments**

### **Precursor Development**

Detailed crystal structure-vapor pressure-melting point studies have been carried out on a series of volatile Ba(hexafluoroacetylacetonate)<sub>2</sub>.polyether MOCVD precursors. Model studies of BaF<sub>2</sub> and Ba<sub>2</sub>Ca<sub>1</sub>Cu<sub>2</sub>O<sub>x</sub> film growth in a horizontal, warm wall reactor demonstrate that precursor transport is diffusion-limited and that film growth is mass transport-limited. Hence, measurements of precursor vaporization rate by vacuum TGA combined with the above information allow expeditious "dialing in" of film growth parameters include circled part on next page here. We have now prepared a new family of fluorine-free alkaline earth (Ba, Sr, Ca) precursors that look very good in terms of volatility and film growth characteristics. Scale-up to be followed by growth demonstrations, distribution to HTMA participants, and transition to manufacture are planned. New precursors for group 4 and



lanthanide metals have also been developed which are superior to previous materials in terms of volatility, thermal stability, and low melting point. Samples of our precursors have been supplied to STI, NRL, and TCSUH for film growth studies. A licensing agreement to manufacture our precursors was signed with Medichem, Inc.

### **Dielectric Buffer Film Growth**

Epitaxial films of the low-, YBCO-lattice-matched/thermal expansion-matched dielectrics LaSrGaO<sub>4</sub> and PrSrGaO<sub>p</sub> have been grown on several substrates by MOCVD. Microstructure and interface properties have been characterized by X-ray diffraction, TEM, SEM, and AFM. Film rms roughness as low as 1.1 nm have been achieved. POMBE growth of YBCO on these dielectrics reveals that superior films (T<sub>c</sub>, J<sub>c</sub>, rms roughness) are produced on LaSrGaO<sub>4</sub> which has a closer YBCO lattice match. Greatly improved MOCVD growth routes to epitaxial CeO<sub>2</sub> and YSZ have also been developed.

### **In-plane Orientation Control of Film Growth**

Thin films of (001) YBCO are grown on epitaxially polished (001) MgO by pulsed organo-metallic beam epitaxy. The in-plane orientation of the film is controlled by the thickness of a BaO layer, grown <I>in situ</I>, prior to the YBCO growth. For thin BaO layers ( $\leq 0.07 \times 10^{15}$  Ba/cm<sup>2</sup>) the films grow [110]YBCO||[100]MgO. For thick BaO layers ( $\geq 1.1 \times 10^{15}$  Ba/cm<sup>2</sup>) the films grow [100]YBCO||[100]MgO. On the other hand, for YBCO films grown on low energy Ar<sup>+</sup> ion sputtered MgO surfaces with a thin BaO layer ( $\sim 0.7 \times 10^{15}$  Ba/cm<sup>2</sup>) the in-plane orientation is [100]YBCO||[100]MgO. A mechanism that relates the change to YBCO in-plane orientation to a change in the structure of the initial BaO layers with BaO thickness has been developed. In addition, in-plane junction devices are being fabricated and studied.

### **Interface/Dielectric Science**

a. We have developed a low temperature CVD approach to growing MgO films, and in preliminary work showed that the growth procedures are applicable to all - CVD fabrication of Tl-2212/MgO/Tl-2212 trilayers.

b. We have successfully grown by CVD bilayer films of YBaCuO and YSZ on LaAlO<sub>3</sub> substrates. The successful growth of the YBCO films is critically connected to the crystalline quality of the YSZ buffer layer. For low quality YSZ layer, no crystalline YBCO film was grown and instead the growth of a BaZrO<sub>3</sub> layer occurred. However, when a YSZ film with a X-ray rocking curve of 0.7 degree or smaller is grown, crystalline YBCO films can be grown with a very sharp interface as examined with TEM. The critical transition temperature for the YBCO film was measured to be 89.3K.

### **Liquid Source Delivery HTS MOCVD**

Northwestern HTS expertise was combined with ATMI reactor techniques to demonstrate high-quality YBCO films can be grown on Ag-buffered stainless steel. Illinois Superconductor collaborated in the R<sub>s</sub> characterization.

### **Nucleating Unusual/ Useful HTS Phases in MOCVD Growth Processes**

TlBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>9+x</sub> exhibits T<sub>c</sub> values as high as 120 K and excellent magnetic flux pinning characteristics. However, application to coated conductor technologies has been frustrated by the difficulty in growing phase-pure, high-quality films. We have now shown that this can be efficiently accomplished by MOCVD using a fluoride-containing post-anneal.

### **MOCVD Reactor Development**



An advanced HTS/oxide CVD reactor has been constructed. It has sophisticated diagnostics to monitor the microstructural evolution of YBCO interfaces in real time. This reactor will also test new on-line diagnostics for control/optimization of the film growth process. Our current reactor has been retrofitted with additional precursor reservoirs to allow multilayer structures to be fabricated in situ. A third CVD reactor has been completed which will be dedicated to rapid, survey growth experiments with new precursors.